

10/086, 231

**HIGH PURITY GLASS BODIES FORMED BY ZERO SHRINKAGE CASTING****BACKGROUND OF THE INVENTION****1. Field of the Invention**

5           The present invention relates generally to a method for making glass, and particularly to a method for making high purity glass bodies.

**2. Technical Background**

          Integrated circuits (ICs) are fabricated using microlithographic systems. The goal of  
10   IC manufacturers is to produce integrated circuits having linewidths as small as possible. Most of the microlithographic systems currently in use employ transmission optics having an illumination source coupled to an illumination optics assembly. These system components provide a photomask with illumination light. The illumination optics expand and collimate the laser light to thereby homogenize the light intensity. The photomask includes the image  
15   of an integrated circuit disposed thereon. The photomask is positioned between the illumination optics and a projection optical system. The projection optical system projects the image of the integrated circuit onto the semiconductor substrate to thereby expose the substrate. Both the illumination optical system, the photomask, and the projection optical system employ transmission optics. One way of reducing the linewidth in systems that  
20   employ transmission optics is to reduce the wavelength of the laser light source.

          It was once thought the limit of making integrated circuits using transmission optics would be somewhere around one micron. However, with illumination light sources being capable of transmitting much shorter wave lengths, one-tenth micron feature sizes and smaller are currently being produced. For example, KrF lasers, which operate at a wavelength of  
25   248nm, are capable of producing integrated circuits having linewidths approaching 100nm. ArF lasers represent an improvement over KrF lasers, operating at a wavelength of 193nm. With improvements to the transmission optics, integrated circuits can theoretically be produced with linewidths near 70nm. Designers are now considering F<sub>2</sub> lasers. These lasers operate at a wavelength of 157nm. F<sub>2</sub> lasers hold the promise of producing integrated circuits  
30   having linewidths on the order of 50nm.

          While it may be possible to further reduce the operating wavelength of light sources used in illumination systems, the very use of transmission optics is becoming a limiting factor. The problem is that the glass materials currently employed are not transparent at

shorter wavelengths. Integrated circuit manufacturers have seen this problem coming for some time and are investigating ways of overcoming the above described limitations.

In one very promising approach, designers are considering reflective optical microlithographic systems that employ extreme ultraviolet (EUV) illumination sources. EUV systems operate at wavelengths in an approximate range between 11nm and 13nm. Instead of transmitting light through lens systems, reflective optical systems employ mirrors to direct the light onto the semiconductor substrate. The photomasks used in EUV systems are also reflective. Because the wavelengths in EUV systems are so short, any irregularity present on the surface of a mirror will significantly degrade system performance. Thus, the optical blanks used to produce EUV mirrors must be of the highest quality.

Quality optical blanks useful in current microlithographic systems are being produced using a flame hydrolysis process. A mixture of very pure silica precursor and a titania precursor are delivered in vapor form to a flame. The precursors react to form  $\text{SiO}_2\text{-TiO}_2$  soot particles. The soot particles melt in layers forming a solid fused silica optical blank. While this method can be used to produce high quality optical components for optically transmissive devices, this method has drawbacks when it is used to make EUV reflective optical components.

One problem being encountered in the fabrication of mirrors suitable for EUV applications is the presence of striae in the optical blank. Figure 1 is a photograph showing an optical blank 1 made in accordance with the flame hydrolysis process described above. As shown, optical blank 1 includes striae 2 disposed therein. The striae 2 are formed as layers of soot are deposited during the flame hydrolysis process. Striae 2 are less of an issue in photomasks than in optical mirror components. Another problem associated with striae 2 is known as springback. Springback refers to the shape change of a glass object with a non-uniform coefficient of thermal expansion (CTE). The change in shape typically occurs upon removal of material from the glass object. Another problem relates to the presence and distribution of inclusions within the glass. Inclusions are either solid impurities or gaseous bubbles disposed within the glass. The occurrence of inclusions in glass made using the flame hydrolysis process is low, but improvements are always desired especially for EUV applications.

A method is needed to produce optical blanks having substantially no striae and no low frequency thermal expansion variations. A method is needed to produce low expansion glass suitable for various applications including transmission optics over a wide range of

wavelengths. What is also needed is a method for producing EUV compatible optical blanks for use in reflective microlithography. A method is also needed that enables the production of large optical devices without cracking.

5

#### SUMMARY OF THE INVENTION

The present invention relates to a method for producing optical blanks for EUV microlithographic components. The present invention provides a method for producing homogeneous optical blanks having substantially no striae. The method of the present invention produces dense, substantially inclusion free glass. As a result, scattering is substantially reduced when EUV light is reflected from a component produced from the optical blank. Furthermore, the method of the present invention is also advantageous because it enables the production of large optical blanks that are not susceptible to cracking.

One aspect of the present invention is a method for forming a glass body. The method includes providing a glass aggregate. The glass aggregate is mixed with a liquid to form a slurry. The slurry is cast in a mold to form a porous pre-form. The mold includes a porous glass substrate. The porous pre-form is consolidated into a glass object.

In another embodiment, the present invention is a method for forming a glass body. The method includes providing a glass aggregate. The glass aggregate is mixed with a liquid to form a slurry. The slurry is pressure cast in a mold to form a porous pre-form. The porous pre-form is heated to form a glass object.

In another embodiment, the present invention is a method for forming a glass body. The method includes providing glass particles. The glass particles include relatively fine glass soot particles mixed with relatively coarse glass particles. The glass particles are mixed with a liquid to form a slurry. The slurry is pressure cast in a mold to form a porous pre-form. The porous pre-form is heated to form a glass object.

In another embodiment, the present invention is a method for forming a glass body. The method includes providing glass particles, the particles including relatively fine glass soot particles mixed with relatively coarse glass particles. The glass particles are mixed with a liquid to form a slurry. A mold is provided that has a glass substrate. The slurry is pressure cast in the mold to form a porous pre-form. The porous pre-form is consolidated to form a glass object.

In another embodiment, the present invention is a method for forming a glass body. The method includes providing a glass aggregate. The glass aggregate is mixed with a liquid

to form a slurry. The slurry is pressure cast in a mold to form a porous pre-form. The porous pre-form is disposed in a chlorine gas atmosphere heated to a predetermined temperature. The chlorine gas reacts with the impurities for a pre-determined time, whereby the impurities are vaporized and carried out of the porous pre-form. The porous pre-form is consolidated to form a glass object.

In another embodiment, the present invention is a method for forming a glass body. The method includes providing glass particles, the particles including relatively fine glass soot particles mixed with relatively coarse glass particles. The glass particles are mixed with a liquid to form a slurry. The slurry is pressure cast in a mold to form a porous pre-form. The porous pre-form is disposed in a chlorine gas atmosphere heated to a predetermined temperature, the chlorine gas reacting with the impurities for a pre-determined time, whereby the impurities are vaporized and carried out of the porous pre-form. The porous pre-form is consolidated to form a glass object.

In another embodiment, the present invention is a method for forming a glass body. The method includes the step of providing a glass aggregate. The glass aggregate is mixed with a liquid to form a slurry. The slurry is cast in a mold to form a porous pre-form, the mold including a porous glass substrate having the same composition as the glass aggregate. The porous pre-form is consolidated into the glass body.

In another embodiment, the present invention is a method for forming a glass body. The method includes the step of forming soot particles as a by-product of a flame hydrolysis process. The soot particles are mixed with a liquid to form a slurry. Coarse glass cullet is disposed in a mold. The slurry is vacuum cast in a mold to form a porous pre-form. The mold includes a porous glass substrate. The porous pre-form is consolidated into the glass body.

Additional features and advantages of the invention will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from that description or recognized by practicing the invention as described herein, including the detailed description which follows, the claims, as well as the appended drawings.

It is to be understood that both the foregoing general description and the following detailed description are merely exemplary of the invention, and are intended to provide an overview or framework for understanding the nature and character of the invention as it is claimed. The accompanying drawings are included to provide a further understanding of the invention, and are incorporated in and constitute a part of this specification. The drawings

illustrate various embodiments of the invention, and together with the description serve to explain the principles and operation of the invention.

### BRIEF DESCRIPTION OF THE DRAWINGS

5 Figure 1 is a photograph showing an optical blank made in accordance with the flame hydrolysis process;

Figure 2 is a schematic of a system for producing soot particles in accordance with one embodiment of the present invention;

10 Figure 3A is a perspective view of an apparatus for pressure casting a porous pre-form in accordance with one embodiment of the present invention;

Figure 3B shows a porous pre-form fabricated using the apparatus depicted in Figure 3A; and

Figure 4 is a detail view of a mold used in an apparatus for pressure casting a porous pre-form in accordance with another embodiment of the present invention.

15

### DETAILED DESCRIPTION

Reference will now be made in detail to the present exemplary embodiments of the invention, examples of which are illustrated in the accompanying drawings. Wherever possible, the same reference numbers will be used throughout the drawings to refer to the same or like parts.

20

In accordance with the invention, the present invention relates to a method for forming an optical device. The method includes providing glass particles. The glass particles are mixed with a liquid to form a slurry. The slurry is cast in a mold to form a porous pre-form. The porous pre-form is consolidated into a glass object. The method of the present invention produces optical components having substantially no striae and substantially no low frequency compositional variations. As a result, scattering is substantially reduced when EUV light is reflected from a component produced from the optical blank. In one embodiment of the present invention, the glass particles are a mixture of two vastly different particle sizes. The mixture of particle sizes allows efficient particle packing within the slurry and the filter cake. Thus, large glass bodies can be formed without cracking because porosity and shrinkage are minimized during casting and firing. Using larger pieces of glass within the glass mixture allows parts to cast at faster rates because the pore channels are

30

correspondingly higher and the capillary stresses within the parts decrease as the particle size increases.

As embodied herein, and depicted in Figure 2, a schematic of system 10 for the direct production of soot particles using flame hydrolysis in accordance with one embodiment of the present invention is disclosed. System 10 includes a source of silica precursor 14. A carrier gas 16, such as nitrogen, is introduced at or near the base of source 12. A bypass stream of carrier gas is introduced at 18 to prevent saturation of the vaporous stream. The vaporous stream passes through distribution system 20 to manifold 22. System 10 also includes source 24 of the titania precursor 26. Those of ordinary skill in the art will recognize that the titania precursor is used in the fabrication of ULE glass. ULE glass is fused silica glass that includes 6 - 9wt % titania. When HPFS is being produced, no titania precursor is employed. Source 24 also has inlet 28 for a carrier gas that is transmitted through precursor material 26. A bypass stream is introduced at 30. The vaporous stream passes through distribution system 32 to manifold 22.

The silica vapor stream and the titania vapor stream mix in manifold 22. The mixture passes through fume lines 34 to burners 36 mounted in upper portion of furnace 38. The mixed vapor stream is further joined with a fuel/oxygen mixture at burners 36. The vapor stream combusts and is oxidized to form silica-titania particles at a temperature in excess of 1600°C. The particles cool and are directed into collection chamber 40. There the particles form a layer of pure ULE or HPFS soot 42. Great care is taken to maintain chamber 40 such that the soot is free from impurities and contaminants.

In another embodiment, soot particles 42 are formed as a by-product of a flame hydrolysis process used to make the ultra-low expansion (ULE) glass and High Purity Fused Silica (HPFS) glass manufactured by Corning Incorporated. In this embodiment, after the vapor stream combusts and is oxidized, forming silica-titania particles, the particles are directed into a cup in the refractory furnace where they melt to form a porous pre-form. However, a significant portion of the glass particles 42 are deposited in the cup, but rather are drawn out of the furnace where they cool and are collected in a bag house. One problem associated with this method is the presence of many impurities and foreign materials in the bag house. Many of these contaminants find their way into the bag house. The bag house soot has a slightly different composition than that of the preform.

In one embodiment of the present invention, soot 42 is mixed with a coarser glass powder to obtain a glass aggregate. The coarse glass powder is obtained by milling or

grinding glass having the same composition as soot 42. The use of a mixture of two or three vastly different particle sizes has several distinct advantages. Large glass bodies can be formed without cracking because shrinkage is minimized during casting. In another embodiment, the glass aggregate is formed by mixing glass soot, glass cullet, and larger pieces of glass. The mixture of particle sizes allows good particle packing within the slurry. Using larger pieces of glass within the glass mixture allows parts to cast at faster rates because the capillary stresses within the parts decrease as the particle size increases.

In the next step, the glass mixture is mixed with water in a 70-30 weight percent suspension to create a slurry. In one embodiment, an ammonia hydroxide dispersant is added to the slurry.

As embodied herein and depicted in Figure 3A, a perspective view of apparatus 300 for pressure casting a porous pre-form in accordance with one embodiment of the present invention is disclosed. Apparatus 300 includes mold 302 coupled to container 304 by way of vacuum hose 306. Container 304 is coupled to vacuum source 310 by way of vacuum hose 308. In practice, the slurry is poured into mold 302. Vacuum source 310 applies a vacuum to mold 302 and container 304. As a result, water is drawn from the slurry into container 304 thru a glass grit base. The vacuum is applied until the cast pre-form freely releases from mold 302. Subsequently, the cast pre-form is allowed to dry slowly in ambient conditions. Figure 3B is a photograph of a porous pre-form 312 fabricated using the above described method and apparatus.

As embodied herein and depicted in Figure 4, a detail view of casting mold 400 in an apparatus for pressure casting a porous pre-form in accordance with another embodiment of the present invention is disclosed. Mold 400 includes wall portion 402 disposed on porous glass substrate 404. Wall portion 402 is fabricated using a Teflon or plastic material to prevent drying from the side walls. In one embodiment, glass substrate 404 is of the exact composition as the glass body being formed. This is advantageous because it substantially eliminates contaminants. Glass substrate 404 includes a plurality of capillaries and pores 406 disposed throughout. The porous nature of substrate 404 is advantageous because faster casting rates can be achieved by virtue of the capillary action. Substrate 404 is also made using the flame hydrolysis process described above. Referring back to Figure 2, system 10 is modified by disposing a cup or container directly beneath burners 36. After the vapor stream combusts and is oxidized to form silica-titania particles, the particles are directed into the cup where they melt to form a green body. In order to maintain the porosity of substrate 404, the

green body is only partially sintered. The temperature is high enough to pyrolyze the water and organic material out of the mold and lightly sinter the glass aggregate together, but the temperature is not high enough to close the pores.

Referring back to Figure 3A and Figure 3B, after casting and drying at room temperature, porous pre-form 312 must be thoroughly dried to eliminate any residual moisture. The remaining adsorbed water is removed by heating porous pre-form 312 to approximately 1000 °C. One possible furnace schedule used for drying pre-forms 312 involves heating at a rate of 1 °C/min until the temperature reaches approximately 100 °C, followed by heating at a rate of 2 °C/min until the temperature reaches approximately 1000 °C. Subsequently, the furnace is cooled to room temperature. This schedule accomplishes the tasks of drying, organic impurity burnout, and pre-sintering.

If porous pre-form 312 is produced using high purity soot (see Figure 2), no chlorine treatment is necessary. If the bag house soot, formed as a by-product of the flame hydrolysis process, is used to make the ultra-low expansion (ULE) glass and High Purity Fused Silica (HPFS) glass manufactured by Corning Incorporated, then it must be cleaned because it may contain impurities and/or other foreign materials. Inorganic material, as well as organic material are commonly found in the bag house soot. Most of the organic impurities are burned out during presintering, but inorganic impurities remain throughout the process of making the glass.

High temperature chlorine gas treatment is a technique used to remove impurities such as alkalis, iron, and water from porous bodies. To be effective, the chlorine gas must diffuse through the porosity of the part and reach the surface of the soot particles. At high temperatures, chlorine gas reacts with the impurities to form compounds which are vaporized and carried out of the substrate with flowing chlorine and a carrier gas such as helium or oxygen. The chlorine treatment reduces contamination from both the soot forming and the porous pre-form forming processes.

Table I provides an example of a schedule used for chlorine treatment of ULE green bodies. During each chlorine cycle a mixture of 20% helium and 80% chlorine gas flows within the furnace for one hour. The furnace reaches a maximum pressure of about 500 torr. After one hour the chlorine flow is arrested and the furnace is evacuated to about 5 torr with continued helium. The vacuum is maintained for thirty minutes after which another cycle begins. Those of ordinary skill in the art will recognize that modifications can be made to the



schedule provided in Table II. For example, in segment 1, the set point can be higher and nitrogen or oxygen can be used instead of helium.

Table I

Segment	Set Point (°C )	Heating Rate (°C /min)	Conditions
1	825	2	Vacuum w/ minimum He flow
2	825	-----	Up to 6 chlorine cycles
3	Room Temp.	Furnace Cool	Vacuum w/ minimum He flow

5 After chlorine treatment the porous pre-form is consolidated into a glass body by applying heat. In one embodiment, the pre-form is heated to approximately 1650 °C for about ten minutes. The porous pre-form can also be consolidated by sintering using a high temperature electrically heated furnace. The sintering of glass particles is achieved via viscous flow, and is therefore time and temperature dependent. The sintering temperature  
 10 can be between 1000 °C and 1600 °C. One example of a sintering schedule includes heating at a rate of 5 °C /min until the temperature reaches 1400-1450 °C, followed by a more rapid cooling rate of 20 °C /min to the annealing temperature.

15

#### Examples

The invention will be further clarified by the following examples which are intended to be exemplary of the invention.

#### Example 1

Initially, 267ml of NH<sub>4</sub>OH was added to de-ionized water to create a 2 liter stock  
 20 solution. About 700g of aggregate was mixed with the solution to form a slurry. The slurry was pressure cast using the apparatus described above. A vacuum with desiccant was used to remove the water to slowly build up the cast pre-form. After about 24 hours the remaining slurry was poured into a waste container. The pre-form was allowed to remain in the mold with the vacuum applied for a few more hours until the cast pre-form freely released from the  
 25 mold. The mold includes a substrate consisting of glass having the same composition as the aggregate. After removal, the pre-form was allowed to dry slowly at room temperature for

another 24 hours to remove most of the remaining water. Subsequently, the pre-form was heated to approximately 1000 °C to remove any remaining adsorbed water.

The pre-form was chlorine treated by being heated to 1000 °C under flowing nitrogen. Chlorine gas was introduced and three cycles of vacuum were applied. A definition of a chlorine treatment cycle is provided in the description above. The pre-form was removed from the furnace and cooled. Subsequently, the chlorine treated pre-form was heated to 1650 °C for approximately ten minutes and consolidated into a striae free glass body.

#### Example 2

A stock solution was prepared by mixing water with 0.1wt% ammonia. A slurry was prepared by mixing 70wt% soot powder with 30wt% stock solution. The soot used in the aggregate included 7wt% titania. The slurry was further mixed with ULE glass cullet that was crushed to around a 10 to 14 mesh size at a ratio of about 1:1 by weight. The mixture was then poured into a porous mold in such a way as to prevent gas entrapment. The mixture was allowed to dry over a two day period. Subsequently, the pre-form was heated to approximately 1000 °C to remove any remaining adsorbed water.

The pre-form was chlorine treated by being heated to 1000 °C under flowing nitrogen. Chlorine gas was introduced and three cycles of vacuum were applied. A definition of a chlorine treatment cycle is provided in the description above. The pre-form was removed from the furnace and cooled. Subsequently, the chlorine treated pre-form was heated to 1650 °C for approximately ten minutes and consolidated into a striae free glass body.

#### Example 3

This example is virtually identical to Example 2, with the exception of the composition of the aggregate. In this example ULE glass beads were used instead of ULE cullet. The beads were formed using fine glass powder(0.1:µm typical size). The powder was agglomerated by such spray drying or forming droplets of a slurry on filter paper. The resulting material was consolidated into beads by heating in a clean atmosphere at temperatures of around 1400 °C.

It will be apparent to those skilled in the art that various modifications and variations can be made to the present invention without departing from the spirit and scope of the invention. Thus, it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.